

SUPERCRITICAL DESULFURIZATION RATES OF WHOLE AND TREATED COALS.

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Introduction

Growing concern over the environmental effects of acid rain has resulted in increased interest in development of precombustion removal of sulfur from coal. Most coals are not in compliance with the recent requirements which call for reduction of sulfur emissions from various fuel sources. Under proposed guidelines, even low sulfur, western bituminous coals require some cleaning to meet new source standards of 1.2 lb. of SO_2 per million Btu's and 90% reduction in sulfur content of the coal on a concentration basis.

Typically, Illinois Basin coals contain more sulfur than coals from other coal bearing regions. In order for typical Illinois coals to meet EPA guidelines, some organic sulfur must be removed, in addition to most of the pyritic sulfur. Almost all Illinois coals contain greater than 1% organic sulfur, with most containing more than 2% [1].

The Department of Mechanical Engineering and Energy Processes at Southern Illinois University is developing a desulfurization process to remove both organic and inorganic sulfur from coal without deleteriously affecting key combustion properties [2]. This process employs alcohols under supercritical conditions. The coal/alcohol mixtures produce a clean solid product with an acceptable sulfur content, a high Btu gaseous product and coal derived liquids.

Supercritical fluid extraction of coals has been reported previously, as a method for the production of liquid fuel products from coal under mild conditions, and as a medium for selective desulfurization of coal [2-4]. Alcohols are expected to exhibit greater solubility for polar organic molecules because of hydrogen bonding and dipole attractive forces. They also provide the opportunity for chemical reactions during the extraction because of the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. In addition, enol rearrangements [5] may play a role in desulfurization.

As reported previously [4], different supercritical reaction conditions produced different extents of desulfurization of coals (33.9-65.7%). However this work concentrated on Illinois Coals. The variable desulfurizations probably result from differences in extents of conversion of the pyritic sulfur (to various alteration products, such as pyrrhotite), [4] as well as organic sulfur functionalities (thiophenol, sulfide, and thiophene)

to light gases such as dimethylsulfide, hydrogen sulfide and methylmercaptans. Although the exact mechanism of the methanol/sulfur functionality reactions are not known, the reactions are believed to be complex, involving hydrogen donation by the alcohol, as well as nucleophilic substitutions.

The overall objective of this study was to gain a better understanding of the supercritical alcohol/coal desulfurization process. Initial development of the supercritical desulfurization process utilized a batch reactor system [4]. Recently, microreactor system has been developed, which is similar to tubing bombs developed by Neavel [6], for coal liquefaction studies. This new system has several advantages over the batch reactor system and approximates more closely the operating conditions of the continuous reactor. Using the microreactor system, the heating and cooling times were reduced compared with those required for the batch reactor. This reduction of heating and cooling time, from 60-120 minutes in the batch reactors to 2-3 minutes in the microreactors, is anticipated to give a better understanding of the reaction kinetics under supercritical conditions. The microreactors are designed to provide a uniform temperature within the reactor and allow precise measurements of temperature. Previous optical characterization of the batch reactor residues suggested that mass and/or heat transfer resistance might be present in the batch system [4].

This paper describes the desulfurization of various coals in supercritical methanol. The objective of the study is to determine the effect of coal properties and treatment of coals on desulfurization rates in supercritical methanol. The effects of KOH addition on desulfurization rates is discussed. Other treatments such as physical cleaning and acid demineralization are reported in an associated paper [7].

Experimental

The eight samples studied in this investigation were obtained from the Argonne Premium Coal Sample Bank. The analysis are reported in Table 1. These samples ranged in rank from Lignite to Low Volatile Bituminous and ranged in Sulfur contents from 0.5 to 5.0% on a dry basis. The values reported in Table 1 were calculated from as received basis as reported by Dr. Vorres, the manager of the sample bank.

For some experiments, the coal was treated with KOH. In these experiments, the coal was soaked overnight in a 5% KOH solution of alcohol.

The reaction of coal with methanol was carried out using a microautoclave system. The apparatus consisted of a 10 cc. stainless steel microautoclave linked to a metering valve and a quick disconnect fitting by high pressure tubing. The reactor system was attached to an automatic shaker supported above a fluidized sand bath. The shaker allowed the autoclave to be agitated during reaction to ensure uniformity of reaction. The fluidized sand bath was temperature stability. Pressure was monitored by an Omega pressure transducer connected to the reactor through a two way valve.

Supercritical Reaction

The microautoclaves were first flushed with nitrogen to remove any oxygen present. The reactors were then charged with coal (1 g.) and methanol (2 g.). Further pressurized flushings with nitrogen were carried out to ensure the removal of oxygen after the microautoclave had been sealed. The valve was opened after successive flushed to release the pressurized nitrogen. The charged microreactors were then attached to an automatic shaker held above a sand bath, as shown in Figure 1. The fluidized sand bath was the raised, so as to fully submerge the reactor in the fluidized sand, which had been preheated to the desired temperature. The shaker was then switched on for the desired reaction time (30, and 60 minutes).

Following reaction, the sand bath was lowered and the reactors removed from the shaker. The reactors were vented by slowly opening the metering valve. After the valves had been opened fully for approximately one minute, the reactors were then quenched in a water bath.

The solid residues were removed from the reactors, ground, and then dried in a vacuum oven at 95°C for approximately 90 minutes. The reactors were cleaned after each run, using acetone in an ultrasonic bath to remove tarry residues. Total sulfur analysis was carried out on all of the solid residues. Desulfurization can be calculated on a concentration or weight basis. The results in this paper are reported on a concentration basis. A concentration basis would be used by the EPA if the 90% removal requirements were to be applied. The weight basis is useful in understanding sulfur incorporation and coal vaporization. The two basis can be calculated as follows:

$$\begin{aligned}\%S \text{ Removed}(\text{conc.}) &= (\%S \text{ Raw Coal} - \%S \text{ Product}) / \%S \text{ Raw Coal} \\ \%S \text{ Removed}(\text{wt. \%}) &= (\text{wt. S Raw Coal} - \text{wt. S Product}) / \text{wt. S Raw Coal}\end{aligned}$$

DESULFURIZATION OF COALS OF VARIOUS RANKS

Desulfurization results obtained on the Argonne Premium samples are listed in Table 2. The coals are listed in approximate rank order from left to right. Results are listed for a moderately severe temperature of 400 C, and a high severity temperature, 450°C. Reaction times of 30 and 60 minutes were studied. Results are also listed for tests conducted with and without KOH present.

In general, desulfurization results decrease from left to right indicating a tendency for sulfur to be less removable as rank increases. For example, the data listed for no KOH, 400°C, and 30 minutes of reaction time shows that the sulfur removal in the lignite is an order of magnitude greater than for the low volatile bituminous coal. This relationship can be seen in Figure 1. Since more weight loss is obtained in the lower rank coals, the relationship is more pronounced when the weight percent basis is used. The scatter in the data shown in Figure 1 also decreases when data are viewed on the weight percent basis. However, there is some variability in the relationship within the high volatile rank range even when weight factors are taken into account. Muchmore et al[3] have reported that the Organic to pyritic sulfur ratio has an effect on desulfurization of Ill.

basin coals and Hippo et al[7] have reported that physical cleaning increases subsequent desulfurization response. Thus variation in total sulfur, pyritic to organic sulfur ratio, and mineral content and composition might explain some of the observed variations.

Results from the tests conducted at 400°C at 30 minutes reaction time yield information on rates of sulfur removal. Two additional factors need to be considered. These factors are the maximum desulfurization obtainable and the selectivity of the sulfur removal. Although the test conducted thus far can not answer these questions entirely, they do shed light on the problems each coal has in obtaining the desired 90% removal level. For example the lignite coal yielded a 70-75% reduction in sulfur on a concentration basis and 85-89% reduction on a weight basis for the 450°C tests without KOH addition. But, this was obtained at 48% weight loss. Energy balances have not been conducted, but the 48% weight loss must represent a significant loss of energy to the vapor phase. This is not necessarily a detriment since the liquid in gases could be sold after they were cleaned. But, the weight losses complicate the analysis of the data and the determination of the optimum desulfurization conditions.

For 5 of the eight coals examined, the maximum sulfur removal in the absence of KOH occurred at 450°C and 30 minutes of reaction time. The other three coals yielded higher sulfur removals on a concentration basis at 400°C. The difficulty in specifying conditions at which maximum sulfur removals will occur arises from many factors. The major factor is that sulfur removals on a concentration basis can decrease with increase reaction time and temperature. Examples of this can be seen throughout Table 2. The decrease in the sulfur removal can occur for two reasons. One, incremental weight losses results in low selectivity towards additional sulfur removal and an increase in the selectivity toward hydrocarbon removal. For example, results at 450°C for 30 and 60 minutes reaction time in the absence of KOH for coal 6 shows a decrease in the concentration of sulfur removed even though on a weight basis the total sulfur removal has increased from 35 to 39%. The second reason for decreases in the sulfur removal on a concentration basis is due to incorporation of sulfur as has been reported previously[8]. For example, at 60 minutes of reaction time for 400°C and 450°C in the presence of KOH; coal 5 decreases in sulfur removal from 43% to -2% on a concentration basis. The weight % sulfur removed also decreases from 45% to 3%.

Both of these factors appear to be somewhat dependent on coal rank. The low rank coals appear to be more susceptible to loss of sulfur removal due to loss of selectivity than the high rank coals. For example the subbituminous coal in the absence of KOH shows a decrease in the sulfur removal at 450°C between the 30 and 60 minutes of reaction time despite an increase in the total sulfur removed. Furthermore when the lower rank coals show some decrease in the total weight of sulfur removed; it is usually small in magnitude. The higher rank coals show the exact opposite trend. When a decrease in sulfur removal on a concentration basis is observed it is always as a result of a decrease in the weight of sulfur removed. In addition as rank increases, the relative amount of sulfur that is incorporated back into the coal residue increases. Thus, Rank appears to be one factor that influences selectivity of the sulfur removal and the incorporation of the sulfur.

The above observation may be the result of the experimental conditions employed. As has been reported previously, the extent of the sulfur incorporation is extremely condition sensitive[8]. In addition, equilibrium considerations may be dominant in the system. If so, then total sulfur in the vapor phase might contribute to the sulfur incorporation. Other factors might include the composition of the minerals present and the reactions that the minerals undergo during the extraction process. Pyrite and other minerals might catalyze the incorporation phenomena. The incorporation might be temporary as observed by Murdie et al[8] or at the high severity the incorporation may be permanent. The cause of the incorporation is not understood. It may be associated with phase changes reducing the solubility of the sulfur compounds in the supercritical vapor, or it may be due to the reaction of sulfur compounds in the bulk vapor phase with coal radicals created by the thermal processing of the coal. At mild severity the sulfur may remain active towards removal but at high severity the incorporated sulfur may crosslink and become inactive toward the alcohol.

EFFECT OF KOH ADDITION

The effect of KOH can also be seen in Table 2. At almost every condition KOH increases sulfur removal. The few results where KOH does not increase sulfur removal is where extensive sulfur incorporation is noted. Since KOH does not effect the global activation energy[8], the increase sulfur removals must be due to physical effects. One possibility is that KOH may function as a crosslinking agent. This is supported by the well known tendency of KOH to reduce fluidity, agglomeration, and swelling. Or KOH may serve as a cracking catalysts providing increase amounts of sulfur sites for reaction. In order to have no effect on the activation energy, the cracking reaction must be much faster than the sulfur removal reactions. This idea is supported by the large effects that KOH has on coals 5 and 6. The data also suggest that KOH plays a role in the incorporation of sulfur. The extent of sulfur incorporation is much greater in the presence of KOH. This may be simply that KOH provides a larger concentration of sulfur compounds in the vapor phase at the conditions that incorporation occurs. Or, the KOH may play a direct role in adding sulfur to coal free radicals and thus providing a higher probability for sulfur to be affixed by crosslinking.

CONCLUSIONS

This study has shown that:

- 1) Desulfurization is rank dependent.
- 2) Other coal properties effect desulfurization.
- 3) KOH increases sulfur removal and sulfur incorporation.
- 4) Maximum desulfurization is difficult to access.
- 5) Sulfur removal is condition dependent.
- 6) Sulfur removal selectivity varies throughout the process.
- 7) Optimization for maximum selectivity and removal requires an understanding of sulfur incorporation kinetics and mechanism as well as removal mechanisms and kinetics.

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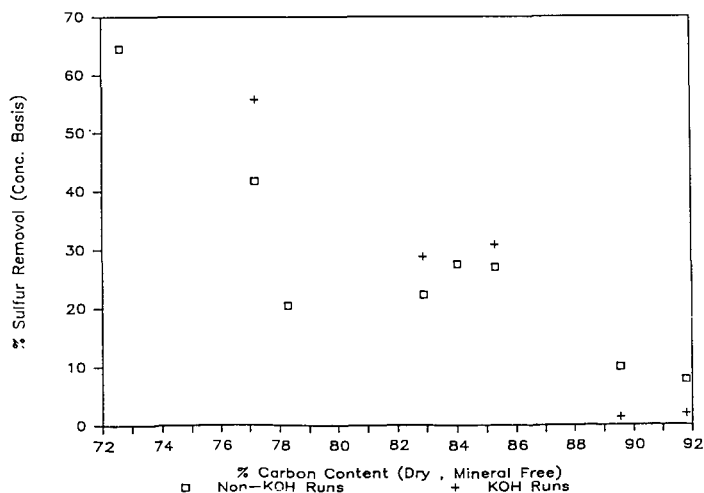


Figure 1. DESULFURIZATION IS A FUNCTION OF RANK: The data in the graph is for supercritical methanol extraction at 400°C and 30 minutes reaction time. Both KOH and Non-KOH runs indicate that sulfur is difficult to remove as rank increases.

TABLE I

Properties of Coals* Used in Supercritical Methanol Extraction Tests

COAL	UPPER FREPORT	WYODAK	ILL	NO.6	PITTSBURGH NO.8	POCAHONTAS NO.3	BLIND CANYON	LEWISTON STOCKTON	BEULAH ZAP
SAMPLE NO.	1	2	3	3	4	5	6	7	8
(dry)									
ULTIMATE									
ANALYSIS									
CARBON	75.46	69.35	65.2	65.2	75.6	86.6	74.1	65.1	67.15
HYDROGEN	4.72	2.42	4.82	4.82	5.34	4.48	5.7	4.38	7.89
NITROGEN	1.40	1.05	1.19	1.19	1.49	0.93	1.30	1.03	0.92
SULFUR	2.49	0.66	5.05	5.05	2.25	0.61	0.59	0.70	0.78
OXYGEN	2.83	17.57	6.04	6.04	5.88	2.48	13.65	8.98	16.73
(by diff.)									
PROXIMATE									
ANALYSIS									
ASH	13.10	8.95	17.7	17.7	9.44	4.90	4.68	19.81	6.53
VOLATILE									
MATTER	27.6	33.95	30.92	30.92					
SULFUR									
FORMS									
SULFATE	0.01	0.007	0.008	0.008	0.01	0.003			
PYRITE	1.98	0.12	2.78	2.78	1.39	0.178			
ORGANIC	0.50	0.54	2.26	2.26	0.85	0.427			
CALORIC									
VALUE	13,362	11,646	10,290	10,290					
MINERAL									
MATTER**	15.73	10.17	21.31	21.31	11.32	5.62	5.40	22.5	7.5

*Properties of Argonne Coals Supplied by Karl Vorres except Sulfur Contents which were determined at SIUC.

**PARR Formula.

TABLE II

Coal No. Rank	DESULFURIZATION OF ARGONNE PREMIUM SAMPLE COALS IN SUPERCRITICAL METHANOL									
	8 Lignite	2 Sub-bit	3 High Vol	6 High Vol	7 High Vol	4 High Vol	1 Med Vol	5 Low Vol		

REACTION CONDITIONS
TEMPERATURE TIME
°C MIN.

NO KOH ADDITION

400	30	65	42	22	21	28	27	10	8
400	60	74	47	21	8	30	32	24	17
450	30	75	50	28	19	34	24	29	3
450	60	70	48	26	14	32	28	33	7

KOH ADDITION

400	30		56	29			34	1	10
400	60		61	28	56		32	24	45
450	30		42	35	72		32	37	19
450	60		54	30	66		12		3